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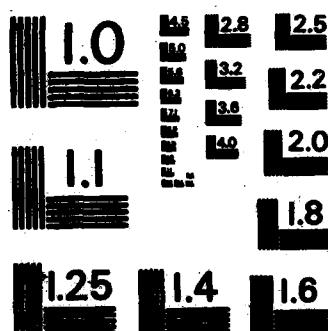
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The technique of Mossbauer Spectroscopy and Nuclear Magnetic Resonance has been used to measure the hyperfine field, the electric quadrupole moment, and the isomer shift of the iron nucleus, the cobalt nucleus, and the samarium nucleus in the presence of different local environments caused by a) the addition and deletion of various constituents, and b) by different heat treatments of the $\text{Sm}_2(\text{Co}, \text{Cu}, \text{Fe}, \text{Zr}, \text{Cr})$ alloys. This was done in order to understand the role of the various substituents and of the metallurgical treatment with a view to gaining insight concerning optimum procedures for the production of improved permanent magnets.

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Extended Theory of Coercive Force due to Domain Wall Pinning., D. I. Paul,
Jrnl. of Appl. Physics, 53, 2362 (1982).

General Theory of the Coercive Force due to Domain Wall Pinning, D. I. Paul,
Jrnl. of Appl. Physics 53, 1649 (1982).

Contrasts in the Coercivity of SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ Type Permanent Magnets, H. A.
Leupold, F. Rothwarf, J. T. Breslin, J. J. Winter, A. Tauber, and D. I. Paul,
Jrnl. of Apply Physics 53, 2392 (1982)

Hyperfine Interactions of Samarium and Cobalt in $\text{Sm}_2\text{Co}_{17}$, E. Potenziani,
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Domain Wall Pinning in the Hard Permanent Magnet $\text{Sm}_2\text{Co}_{10}\text{Cu}_{1.48}\text{Fe}_{3.16}\text{Zr}_{0.194}$
D. I. Paul, I.E.E.E. MAG 16, 1003, (1980).

Interim Technical Report to ARO (Dec. 1981) re: technical findings. Information therein is contained in scientific publications referenced above.

INTRODUCTION AND STATEMENT OF THE PROBLEM:

It has been noted by the U. S. Army that the new magnetic circuit designs being considered for microwave and millimeter wave tubes require permanent magnets with high energy products, i.e., $(BH)_{\text{max}}$ greater than 30MGOe, low reversible temperature coefficients of magnetization, and linear demagnetization curves. To attain such materials, preliminary studies were made by the U. S. Army at Ft. Monmouth (ET&DL) on the alloy $\text{Sm}_2(\text{Co}, \text{Cu}, \text{Fe}, \text{Zr}, \text{Cr})_{17}$. This type of alloy, without the chromium, was first developed by T. Ojima and coworkers (Jpn Jrnl Appl. Phys. 16, 671 1977) in Japan. They determined, strictly on a heuristic basis, that zirconium increased the coercive force and that the optimum alloy was $\text{Sm}_2\text{Co}_{10}\text{Fe}_{3.16}\text{Cu}_{1.48}\text{Zr}_{0.194}$. It had an energy product of 30MGOe for a particular heat treatment. F. Rothwarf, et al, (Jrnl. of Appl. Phys. 50, 2352, 1979) of the U. S. Army, Ft. Monmouth, investigated the effects of Mn and Cr substituents and a different heat treatment on the saturation magnetization, the temperature coefficient, and the anisotropy field. They noted a large increase in the magnetic anisotropy with an optimum value at room temperature of $x=0.5$ for chromium.

We have used the technique of Mossbauer Spectroscopy and Nuclear Magnetic Resonance to measure the hyperfine field, the electric quadrupole moment, and the isomer shift of the iron nucleus, the cobalt nucleus, and the samarium nucleus in the presence of different local environments caused by a) the addition and deletion of various constituents, and b) by different heat treatments of the $\text{Sm}_2(\text{Co}, \text{Cu}, \text{Fe}, \text{Zr}, \text{Cr})$ alloys. We have done this in order to understand the role of the various substituents and of the metallurgical treatment with a view to gaining insight concerning optimum procedures for the production of improved permanent magnets.

SUMMARY OF MOST IMPORTANT RESULTS:

All results including those listed below have been reported in the above referenced scientific journals.

The basic findings, as deduced from the Mossbauer and zero-field spin-echo NMR experiments can be collected into and discussed as five main points. They are:

1. The addition of copper, as shown by ^{59}Co NMR, causes a precipitation of free cobalt and a subsequent "stiffening" of the domain wall. The Fe 2:17 Mossbauer data show a large increase in the amount of free iron while both the NMR and the Mossbauer data on the 2:14.8 alloys show the formation of an Fe-Co phase. The

SUMMARY OF MOST IMPORTANT RESULTS: (Continued)

lack of an Fe-Co phase in the stoichiometric 2:17 alloys comes about from a lower solubility of Fe-Co in the 2:17 alloys and a smaller percentage of iron relative to cobalt in the Fe-Co phase (thereby decreasing the signal-to-noise ratio of a Mossbauer spectrum.)

The increased stiffness of the domain walls can be explained by the copper replacing the transition metal atoms of the 1:5 phase, thereby degrading its magnetic properties - the end result of which is a stiffer domain wall and a larger coercive force. Step heat treatment of copper containing alloys generally results in an iron diffusion out of the 1:5 phase. This, in accordance with experimental evidence of the greater solubility of copper in the 1:5 phase relative to 2:17) reinforces this explanation. Further, the lower than usual hyperfine fields of the 2c and 3g sites of the 1:5 phase, as determined from Fe Mossbauer on our 2:14.8 alloy are consistent with a replacement of transition metal atoms by copper atoms in the 1:5 phase.

2. The addition of iron (normally used to increase B_r) causes the formation of an Fe-Co phase when copper is present unless other action is taken to suppress its formation (such as adding zirconium plus a step heat treatment or chromium. This iron also causes a precipitation of free cobalt to occur and decreases the intensity of the Co-Co pair lines as observed by Co NRM. The Co-Co pairs occupy a samarium crystal site in the 2:17 phase. A substantial decrease in the amount of Co-Co pairs is very desirable because of the increased anisotropy which would result from the greater occupancy of these sites by samarium atoms.

It is interesting to note that there was no Fe-Co phase found in the 2:17 alloy $\text{Sm}_2\text{Co}_{12.1}\text{Cu}_{1.6}\text{Fe}_{3.3}$. This indicates that the two phase structure is not favorable at high temperatures (1180°C., the temperature from which the alloys are quenched). An Fe-Co phase, in addition to free iron and cobalt, would be expected in the case of 2:17 alloys as a result of the formation of some 1:5 phase.

3. The effect of zirconium and a step heat treatment is the complete suppression of the Fe-Co phase and a further enhancement of iron diffusion out of the 1:5 phase and into the 2:17 4f crystal site - thereby decreasing the planar anisotropy contribution of this site and increasing the axial anisotropy of the 2:17 matrix. This, in conjunction with the Sm NMR result that the zirconium does not change the samarium hyperfine fields (the zirconium is going into the 1:5 phase, replacing a samarium atom) clearly confirms that the magnetic properties of the 1:5 phase are degraded while those of the 2:17 matrix are enhanced - causing a more effective pinning of the domain walls in agreement with the experimentally observed increase in coercive force. Without a step heat treatment, the only beneficial effect of a zirconium addition is a partial decrease in the amount of detrimental Fe-Co phase.

SUMMARY OF MOST IMPORTANT RESULTS: (Continued)

It has been postulated that the chemical redistribution of the transition metal atoms occurs during the 400°C portion of the step heat treatment. Although the 400°C portion of the step heat treatment was not tested solely, it can clearly be seen that the iron content of the 2:17 phase increases relative to that of the 1:5 phase upon step heat treatment - strongly supporting the previous postulate.

We also note the small amount of paramagnetic impurity which was detected by Fe Mossbauer spectroscopy. A recent study by Hadji-panayis et al has determined that besides the magnetic phases found in a 2:14.8 alloy, there are also non-magnetic copper-rich precipitates. Although these precipitates have eluded efforts to determine their exact crystal structure and micro-composition up to this time, it is postulated now that the paramagnetic impurities detected in our work and the non-magnetic precipitates found by Hadji-panayis et al are one and the same.

4. The addition of chromium to this same sample sans the zirconium, $\text{Sm}_2(\text{Co,Fe,Cu})_{14.8}$, completely suppresses the Fe-Co phase but does little to affect the iron population of the 2:17 4f crystal site. The addition of chromium to $\text{Sm}_2(\text{Co,Fe,Cu})_{14.8}$ with a step heat treatment is very effective at facilitating iron diffusion out of the 1:5 phase but the 4f site population remains approximately constant. Therefore, there should be no enhancement of anisotropy by preferential crystal site substitution. In this way, it can be seen that the chromium performs only partially that which zirconium is known to do, i.e., facilitate iron diffusion out of the 1:5 phase and into the 2:17 phase (especially the 4f site of the 2:17 phase). The increase in anisotropy upon the addition of chromium to these rare earth-cobalt alloys can be attributed to band structure changes but the resulting slight increase in coercivity is certainly due to the decrease in the iron content of the 1:5 phase as detected in this work.

5. The addition of both chromium and zirconium simultaneously to $\text{Sm}_2(\text{Co,Fe,Cu})_{14.8}$ causes an increase in the amount of iron in the 2:17 phase relative to the 1:5 phase and a substantial increase in the iron population of the 2:17 4f crystal site. This indicates that although the addition of chromium and a step heat treatment is very effective at facilitating iron diffusion out of the 1:5 phase, the zirconium is needed to incorporate this iron specifically into the 2:17 4f crystal site. The chromium effectively serves to enhance the "zirconium effect" of paragraph 3.

The manner in which this is done can be explained by looking at the results of Rabenberg et al. Although their alloys did not contain chromium, they believed that the "Z" phase plates, a zirconium rich 1:3 phase, served as highly efficient diffusion paths for the transition metals. The enhanced diffusion of transition metals upon the addition of both zirconium and chromium is caused

SUMMARY OF MOST IMPORTANT RESULTS: (Continued).

by the chromium further increasing the diffusivity of these "Z" phase plates. These "Z" phase plates tend to be rich in copper, zirconium, and probably samarium. It is probable that the paramagnetic impurities detected by our FeMossbauer spectroscopy, the non-magnetic precipitates found by Hadjipanayis (See #3 above), and the Z phase plates of Rabenberg et al are all one and the same. The site population changes and enhanced diffusivity that occurs as different elements are added is also caused by the natural minimization of the strain energy due to lattice misfit between the different phases and the fact that the equilibrium compositions of the different phases at 400°C are more dissimilar than those found at the higher temperatures of the step anneal heat treatment. Different alloying agents and heat treatments cause the a and c lattice parameters to vary differently and diffusion of different elements will halt upon reaching a minimum in the stresses which are caused by the lattice mismatch.

Important effects in regard to the enhancement of the magnetic properties of these alloys can be related to the individual time spans of the low temperature step heat treatment. One would prefer a 2:17 cell size of about 1000Å and a 1:5 cell boundary of about 50Å, thus ensuring that the appropriate diffusion processes and domain wall pinning effects will occur. This requires a short heat treatment at 850°C since the cell structure coarsens during this particular step of the heat treatment. In contrast, diffusion which occurs primarily at 400°C - 600°C is a slow process and longer heat treatment times are required to ensure that the diffusion process has been carried to completion. Raising the heat treatment temperature is not the answer since this would also increase the rate of macrostructure coarsening besides the fact that some phases are unstable at higher temperatures. Other alloying agents which diffuse faster but have the same effect as zirconium (that is, enhanced population of the 2:17 4f crystal site) need to be investigated. Some which are being looked at by other investigators are vanadium, manganese, titanium, nickel, and hafnium. Besides the different alloying agents, the "Z" phase plates of Rabenberg et al are suspected of greatly facilitating the diffusion of copper, iron, and samarium. Control of the stability of these phase plates should go a long way towards establishing the ultimate magnetic characteristics of these $\text{Sm}_2(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr}, \text{Cr})_{14.8}$ alloys.

FERROMAGNETIC COERCIVITY OF Sm-Co ALLOYS^{a)}
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ABSTRACT

We have investigated the $\text{Sm}_2(\text{Co,Fe,Cu,Zr,Cr})_{14.8}$ permanent magnets by NMR using both the Co and Sm nuclei and by Mossbauer spectroscopy using the Fe nucleus. A full set of samples was prepared, each containing an additional constituent regarding its predecessor. Samples were analysed, both prior to and after step annealing designed to precipitate out a uniform 2nd phase structure. Our findings are: 1) the addition of Cu precipitates out Fe and Co; noting the shift in the hyperfine field concurrent with this precipitation, one can assume the replacement of these transition metals by the Cu; 2) the addition of Fe causes some substitutional displacement for the Co with the remainder being undissolved in an Fe-Co phase-this increases the remanence; 3) further removal of free Fe is accomplished through the addition of Zr and a subsequent step anneal; thus Zr helps increase the remanence by dissolving Fe; 4) the second, and more important, role of the Zr is known to be an increase in the coercive force, our results indicating that Zr preferentially substitutes in the 1:5 phase-probably replacing the Sm-lowering the magnetic properties of the cellular boundary 1:5 phase, causing it to exert a more effective pinning of the domain walls, in agreement with experimental findings; 5) the addition of Cr with Zr causes the preferential substitution of Fe into the 4f site of the 2:17 phase, thereby increasing the anisotropy and facilitating the removal of the Fe-Co phase.

This represents one of the first times that the functions of the constituents of a complex intermetallic alloy has been able to be analysed on a microscopic basis by resonance techniques.

INTRODUCTION

The family of compounds based on $\text{Sm}_2(\text{CoFeCuZrCr})_{14.8}$ is of considerable interest because of its high-energy product, magnetocrystalline anisotropy, and Curie temperature[1-5]. The optimization of the magnetic characteristics of these materials has been done mainly by empirical methods, but the manner by which the different constituents and heat treatments affect the microstructure and magnetic properties is not always known explicitly and is the basic reason for this investigation.

We have performed zero-field spin-echo NMR on the ^{149}Sm and ^{59}Co nuclei at 4.2K and ^{57}Fe Mossbauer at 300K. The resulting Mossbauer and NMR spectra were examined as the alloying agents and heat treatments were varied systematically in an attempt to determine their effect on a microscopic scale. A more detailed NMR examination of the basic $\text{Sm}_2\text{Co}_{17}$ alloy can be found in a previous paper[6].

EXPERIMENTAL

The series of nonstoichiometric 2:14.8 alloys was obtained by induction-melting the proper amounts of 99.9% pure, or greater, metals in a boron nitride crucible under 12 atm of argon backpressure. The 2:14.8 button was subsequently homogenized in an evacuated quartz vessel at 1150°C for four hours and then rapidly quenched. Those alloys containing copper were also subjected to a step heat treatment of 2 hours at 850°C, 1-1/2 hours at 700°C, 1-1/2 hours at 600°C, 2-1/2 hours at 500°C, 5 hours at 400°C, and 11 hours at 280°C. Further treatment of the

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Mossbauer and NMR samples diverge from this point on.

For the NMR sample, the 2:14.8 homogenized button was ground under sodium metal-dried toluene in a conventional ball milling apparatus. The slurry was then vacuum dried and sifted to a 10-40 micron particle size which is large enough to ensure that several domain walls are present in each particle. About 15 grams of this powder were sealed in an epoxy binder and aligned in a magnetic field of several kilogauss while the epoxy was allowed to cure. The magnetic field mechanically rotates each particle so that the net magnetization is parallel to the applied field, thereby giving us a strong domain wall resonance when the rf is applied parallel to this alignment direction.

The NMR equipment and method of echo measurement was similar to that described by Streever and Uriano[7]. All NMR data were obtained at 4.2K using an exposed tip low temperature dewar which fitted into the resonant rf cavity.

The zero-field spin-echo spectra were obtained by the conventional method of plotting echo amplitude versus frequency while keeping pulse width (1-4 μs) and pulse separation (10-40 μs) constant. Because of the short relaxation times involved (50-200 μs), the sample was never fully saturated, even at high pulse repetition rates. The resulting echo spectra were not corrected for the frequency dependence of the induced echo signal and nuclear polarization. A total correction was made, however, when determining the relative percentage of a particular peak to a total spectrum. As such, all the relative percent intensities quoted herein are local to a particular spectrum.

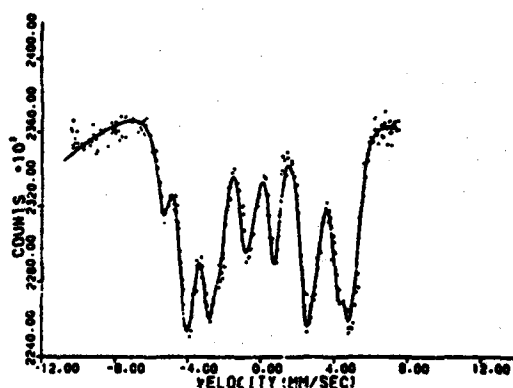
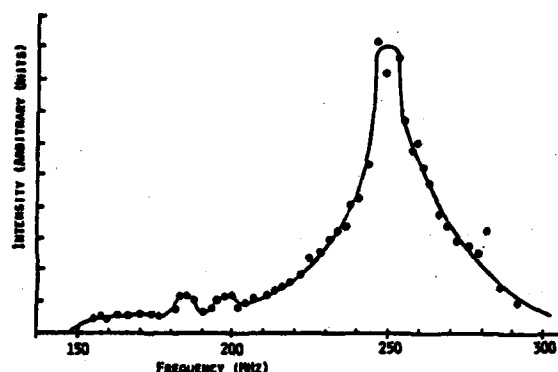
For all the Mossbauer samples, isotope enrichment was necessary because of the low natural abundance of the ^{57}Fe isotope and the high complexity of the spectra. Our samples were of about 30 mg/cm-cm thickness.

The Mossbauer equipment used consisted of a conventional constant acceleration transducer with a 10mCi ^{57}Co on rhodium radioactive source and an argon gas proportional counter. The resulting spectra, which, in some cases, consisted of as many as 49 overlapping Lorentzian lines, were analysed by computer [8] and graphical[9] methods. We used the relative magnitudes of the hyperfine fields, as well as their relative intensities in assigning specific lines to the different crystal sites.

RESULTS AND INTERPRETATION

Some typical NMR and Mossbauer spectra are shown in Figures 1 and 2. To help clarify the cobalt and samarium NMR discussion, we will first explain a few of the terms used: 1) cobalt site lines refer to the four lines due to the four inequivalent cobalt sites of the 2:17 phase; 2) free cobalt lines refer to the lines due to free cobalt, both hexagonal and cubic phases; 3) Fe-Co lines refer to lines originating from an Fe-Co impurity phase.

There are several important points that must be kept in mind as one examines these spectra. First, the NMR signal which we detect comes from the domain walls; as such, both the enhancement factor and the relaxation times are inversely dependent upon the difference in the magnetic "stiffness" (anisotropy and exchange) between the region in which the domain wall lies and the pinning phase[10-12]. Because the 1:5 boundary phase is nucleation-controlled and is of the order of the wall width, we believe that our NMR signal originates from the 2:17 host matrix. Second, the NMR lines originating from the



Fe-Co phase have frequencies of approximately 230 MHz[13]. The exact frequencies and number of peaks depend upon the amount of disorder present and the relative amounts of iron to cobalt. Third, those lines due to free cobalt, of both hexagonal and cubic structures, have frequencies from 215 to 230 MHz[14-16]. Fourth, the resonance lines in the 115-195 MHz range are due to the four inequivalent cobalt sites. Those lines in the 480-650 MHz range originate from the rare-earth sites: one in the rhombohedral structure R3m and two sites in the hexagonal structure P63/mmc. Fifth, because of the short relaxation times for these sites (on the order of 100 μ s), especially the rare-earth site, the resonance lines can become undetectable quite easily once the domain wall enters a magnetically hard region.

Upon the addition of zirconium to $\text{Sm}_2\text{Co}_{14.8}$, the disappearance of the four cobalt site lines (down to a small background) was observed along with the appearance of some free cobalt. The traces of the four cobalt site lines which remain show that their hyperfine fields have not changed. The Sm NMR spectrum shows that the addition of zirconium does not change the samarium hyperfine fields. These facts show that the zirconium goes in substitutionally for the samarium. We have also observed in our work that the Co and Sm NMR spectra of the $\text{Sm}_2\text{Co}_{17}$ and $\text{Sm}_2\text{Co}_{14.8}$ alloys show no difference implying that the domain walls responsible for the NMR signal lie in the 2:17 phase. Thus our lack of change of the hyperfine fields upon the addition of zirconium further implies that the zirconium enters a 2nd phase rather than the 2:17 phase. The decrease in the intensity of the cobalt site lines could come about from the zirconium degrading the magnetic properties of an existing second phase

(possibly 1:5) and thereby "stiffening" the domain wall.

The addition of iron to the $\text{SmCo}_{5-14.8}$ alloy results in the precipitation of some free cobalt and the formation of some Fe-Co phase while the samarium hyperfine fields show an expected decrease. This comes about because both cobalt and iron have a negative contribution to the samarium hyperfine fields by means of the RKKY interaction, with iron having the larger negative contribution.

The addition of copper to the $\text{Sm}_2\text{Co}_{11.67}\text{Fe}_{3.16}$ alloy with a step heat treatment results in the complete disappearance of the cobalt site lines due to the increased rigidity of the domain walls. Relaxation times are now too short to obtain any further samarium NMR data for the more complex alloys.

The addition of zirconium to $\text{Sm}_2\text{Co}_{10.19}\text{Fe}_{3.16}\text{Cu}_{1.48}$ with a step heat treatment results in the complete suppression of the Fe-Co phase. An interesting effect is observed upon the addition of chromium to this zirconium containing alloy without a step heat treatment: the Fe-Co phase, which previously required a step heat treatment of the chromium deficient alloy, is suppressed. Also, the cobalt site lines reappear implying a "softening" of the domain wall, i.e., the anisotropy of the 2:17 and 1:5 phases becoming more similar. When we now step heat treat this $\text{Sm}_2\text{Co}_{9.496}\text{Fe}_{3.16}\text{Cu}_{1.48}\text{Zr}_{.194}\text{Cr}_{.5}$ alloy, the cobalt site lines once again vanish, implying a "stiffening" of the domain wall.

Because of the large number of iron Mössbauer spectra, we have summarized the important parameters such as hyperfine fields and site population ratios in Table I. The site intensity data does not compensate for any difference in the recoil-free fraction between sites, but since interest is in the relative change in site population between samples, this is of no concern here.

For the basic $\text{Sm}_2\text{Co}_{11.67}\text{Fe}_{3.16}$ alloy we did not detect any second phase, possibly due to an iron deficiency of this phase. There was some free iron produced.

[illegible]

The addition of copper to the $\text{Sm}_2\text{Co}_{11.67}\text{Fe}_{3.16}$ alloy causes the formation of some Fe-Co phase (also found in the NMR spectra) and some 1:5 phase, regardless of the heat treatment. When we do heat treat this $\text{Sm}_2\text{Co}_{10.19}\text{Fe}_{3.16}\text{Cu}_{1.48}$ alloy, the amount of iron in the 1:5 phase decreases by about 50% while the amount of detac-ted free iron and Fe-Co remains the same. The iron dif-fusing out of the 1:5 phase into the 2:17 phase does not seem to show any preferential site substitution. The reason for the concern of the site populations in the 2:17 matrix is that the improvement in the anisotropy of

iron containing alloys can be explained on the basis of preferential crystal site substitution[17]. The iron atom can go preferentially into the 4f site (Mycroff notation, hexagonal 2:17 phase)- this site normally having a strong planar anisotropy. However, because the iron couples less strongly than the cobalt, the planar anisotropy contribution of the 2:17 phase is decreased. The resulting difference in anisotropy between the 2:17 and 1:5 phases yields a greater coercive force[18].

The addition of zirconium to $\text{Sm}_2\text{Co}_{10.19}\text{Fe}_{3.16}\text{Cu}_{1.48}$ in and by itself lowers the amount of Fe-Co phase by 60% (also seen in the NMR spectra) but increases the amount of free iron (a free cobalt increase was also seen in the Co NMR). The intensities of the 1:5 and 2:17 phase crystal sites remain approximately the same. The step heat treatment of this $\text{Sm}_2\text{Co}_{9.996}\text{Fe}_{3.16}\text{Cu}_{1.48}\text{Zr}_{1.94}$ alloy results in the complete suppression of any Fe-Co phase (as also seen in the Co NMR) and a halving of the amount of free iron. There is also a marked increase in the 4f site population, indicating a decrease in the iron content of the 1:5 phase. This is what one would expect with the higher anisotropy of this alloy.

We have also investigated the effect of chromium on these alloys, with and without zirconium. The addition of chromium to the $\text{Sm}_2\text{Co}_{10.19}\text{Fe}_{3.16}\text{Cu}_{1.48}$ alloy results in the complete suppression of any Fe-Co phase and a small reduction in the amount of iron contained in the 1:5 phase. Upon step heat treatment of this $\text{Sm}_2\text{Co}_{9.69}\text{Fe}_{3.16}\text{Cu}_{1.48}\text{Cr}_{0.5}$ alloy, there is an increase in the amount of free iron and a further reduction of the iron content of the 1:5 phase by about 15%. A small amount of a paramagnetic impurity begins to form, possibly an Fe-Cr or Fe-Cr-Co phase. Since iron is observed diffusing out of the 1:5 phase, this may imply that the iron is going into the free iron or into the paramagnetic phase because the 4f site (sensitive to iron migration) is ideally populated both in the step and non-step heat treated case, i.e., there does not seem to be any iron enrichment of the 2:17 phase.

The addition of chromium to $\text{Sm}_2\text{Co}_{9.996}\text{Fe}_{3.16}\text{Cu}_{1.48}\text{Zr}_{1.94}$ removes all traces of the Fe-Co phase, as was also shown in the Co NMR. This addition also causes the formation of a paramagnetic phase which corresponds to an Fe-Cr, Fe-Zr or similar phase. A large loss of iron from the 1:5 phase is observed when we step heat treat the $\text{Sm}_2\text{Co}_{9.69}\text{Fe}_{3.16}\text{Cu}_{1.48}\text{Zr}_{1.94}\text{Cr}_{0.5}$ alloy, while the 4f site is populated twice as much as it is in the non-step heat treated case. The amount of free iron is halved and the central line due to the paramagnetic impurity shifts position (isomer shift changes) due to a different Fe:Cr or Fe:Zr ratio.

CONCLUSION

Our findings are: 1) The addition of copper, as observed by Co NMR, causes a "stiffening" of the domain wall with a precipitation of free cobalt and iron. We believe that there are two possible scenarios occurring here: a) the copper replaces the transition metal atoms of the 1:5 phase, thereby degrading its magnetic properties resulting in a "stiffer" wall and a larger coercive force. b) the copper goes into the 1:5 phase as precipitates or interstitials and degrades the 1:5 properties. Step heat treatments of copper-containing alloys generally result in an iron diffusion out of the 1:5 phase which would seem to reinforce thought "a" in accordance with other experimental evidence of the greater solubility of copper in 1:5 relative to 2:17[19].

2) The addition of iron, besides raising the remanence, also causes the formation of an Fe-Co phase unless other action is taken to suppress this phase.

3) The effect of zirconium and a step heat treatment is the complete suppression of the Fe-Co phase, further enhancing the diffusion of iron out of the 1:5 phase, and enhancing the iron substitution into the 4f site, thereby decreasing the planar anisotropy contribution of this site and increasing the axial anisotropy of the alloy as a whole. This, coupled with the Sm NMR result of the zirconium possibly going into the 1:5 phase (replacing a samarium atom[20]), would mean that the magnetic properties of the 1:5 phase are degraded while those of the 2:17 host matrix are enhanced causing more effective pinning of the domain walls, in agreement with experimental findings.

4) The addition of chromium to $\text{Sm}_2(\text{Co}, \text{Fe}, \text{Cu})_{14.8}$, regardless of the heat treatment, does little to affect the 4f site population of the 2:17 phase. However, a step heat treatment of this chromium-containing alloy is very effective at facilitating iron diffusion out of the 1:5 phase. The fact that the population of the 4f site remains constant implies that although both zirconium and chromium are effective in causing the diffusion of iron out of the 1:5 phase, zirconium is needed to incorporate this iron into the 4f site. The enhancement of the anisotropy of alloys containing chromium but no zirconium may be due to band structure changes.

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